Spinels Renaissance: The Past, Present, and Future of Those Ubiquitous Minerals and Materials

Static positional disorder in ulvöspinel: A single-crystal neutron diffraction study†

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ABSTRACT

A single-crystal neutron diffraction study of a synthetic ulvöspinel sample of composition FeFeTiO4 was performed to investigate the static positional disorder at the octahedrally coordinated M site. Anisotropic structural refinement was performed in the space group Fd3m against neutron Laue diffraction data collected at 298 K from two millimetric-sized crystals. Initial structure refinements were conducted with Fe and Ti sharing the M site (at 1/2, 1/2, 1/2), and their partial site occupancy was refined. The tetrahedrally coordinated T site (at 1/8, 1/8, 1/8) was modeled as fully occupied by Fe. For both crystals, the final R1 index was about 3% for 9 refined parameters and 129 unique reflections, with no significant residuals.

As the atomic displacement factors obtained were anomalously high, according to the previous experimental findings, Fabc and (Fabc – Fcalc)-difference Fourier maps of the nuclear density were generated. Fourier maps showed a significant minimum located out-of-center of the M site, and indicating a displacement of the Ti4+ from the center of the octahedron. A further test refinement was successfully conducted with two mutually exclusive sites: 36Ti out-of-center (0.49, 0.49, 0.49) and 36Fe on the center (at 1/2, 1/2, 1/2). The resulting displacement of Ti from the octahedral center appears to be shorter than 0.15 Å.

Using bond-valence theory, the out-of-center distortion of 36Ti4+ is interpreted as a result of intrinsic distortions in the ulvöspinel structure. The potential implication of the octahedral distortion on the behavior of ulvöspinel at non-ambient conditions is discussed.

Keywords: Ulvöspinel, crystal chemistry, neutron Laue diffraction, static positional disorder, bond valence theory

INTRODUCTION

Multiple oxides with spinel structure occur as common accessory in many crustal rocks, but are expected to be important components of the mantle assemblages. Their crystal structure and crystal chemistry, along with their thermo-elastic and magnetic behavior in response to the applied pressure (P) and temperature (T), have been the subject of a significant number of experiments for petrological and geophysical implications along with potential technological applications. The general formula of spinels is AB2O4, where “A” and “B” represent, respectively, either bivalent and trivalent cations (giving A2B3+O4) or tetravalent and bivalent cations (giving A4B2+O4). The crystal structure of spinels can be described as a slightly distorted cubic close-packed array of anions, in which the A and B cations are distributed over one eighth of all tetrahedrally coordinated (T) and half of all octahedrally coordinated (M) sites. This cation distribution leads to two types of site populations: (1) the “normal” one, where the A cation occupies the T site and the two B cations occupy the M sites; (2) the “inverse” one, where the A cation is ordered at M and the B cations occupy both T and M (Barth and Posnjak 1932). The spinel structure is cubic (space group Fd3m). The tetrahedrally coordinated cations are located at the special positions 8a (Wyckoff notation; point symmetry 43m), the octahedrally coordinated cations are located at the special position 16d (point symmetry 3m), and the oxygen atoms lie at the special position 32e (point symmetry 3m). The oxygen fractional coordinate (u) is the only variable atomic position in the structure.

Ulvöspinel is an inverse spinel, with structural formula (Fe3+)M(Fe2+Ti4+)O4. Often, natural Ti-rich spinels belong to the solid solution between magnetite, (Fe3+)M(Fe3+Fe2+)O4, and ulvöspinel (Akimoto 1954). A significant number of experiments have been devoted to the site allocation of cations along the magnetite-